

## THERMAL CONDUCTIVITY OF LIQUID METALS

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(Received for publication, November 26, 1941)

**ABSTRACT.** The abrupt decrease in the thermal conductivity of metals observed near the melting point is explained on the assumption that the frequency of vibration of molecules suffers a change near the melting point. The ratio of thermal conductivities in the solid and liquid phases near the melting point is shown to be given by  $e^{\frac{2}{3} \frac{\lambda_m}{K_0 T_m}}$  where  $K_0$  is the Boltzman constant and  $\frac{\lambda_m}{T_m}$  is the entropy of melting. This is found to be in good agreement with observed values. The slight decrease in the thermal conductivity in the liquid phase is ascribed to the disordered state in the liquid.

The thermal conductivity of normal metals in the liquid state just above the melting point is about half as great as that of the solid metal just below the melting point. Certain abnormal metals, however, such as bismuth and antimony which are poor conductors in the solid, increase their conductivity on melting. The abrupt change in thermal conductivity at the melting point has not been explained so far. An attempt is here made to explain such a change from the point of view of modern theory of electronic conduction based on wave mechanics.

From the standpoint of modern theory, the expression for the thermal conductivity of a metal should contain two additive terms, one due to the lattice and the other due to electron conductivity. A. H. Wilson<sup>1</sup> gives the equation as

$$K = \frac{1}{3} \rho c l u + \frac{\pi^2}{3} \frac{n_0 \tau K_0^2 T}{m}$$

$K$  is the thermal conductivity ;  $\rho$  the density,  $c$  the atomic heat,  $l$  the electron mean free path in the lattice ;  $u$  the velocity of elastic waves in the lattice (sound) ;  $n_0$  the number of free electrons per unit volume ;  $\tau$  the "relaxation time" (average time between collisions) ;  $K_0$  the molecular gas constant ;  $T$  the absolute temperature. If we write the equation as

$$\frac{K}{\rho c} = \frac{1}{3} l u + \frac{\pi^2}{3} \frac{n_0 \tau K_0^2 T}{m \rho c}$$

it is in the form  $\frac{K}{\rho c} = \frac{A}{T} + B$ .

This assumes that  $\tau \propto T^{-1}$  and  $lu \propto T^{-1}$  and that  $\rho$  and  $c$  compensate as to their temperature effects.

The equation in this latter form is experimentally verified by data on tin, lead and zinc.<sup>2</sup> Values of  $\frac{K}{\rho c}$  plotted as ordinate against  $\frac{1}{T}$  as abscissa give straight lines with intercepts on the y-axis and these intercepts turn out to be the values of  $\frac{K}{\rho c}$  for the molten state. The conductivity for the molten state includes the residual atomic conductivity as well as that due to electrons. The conductivity of an insulating liquid is very small (1 per cent. or less than that of a conductor). Hence the last term on the right is, very likely, almost entirely electron conductivity. The temperature effect for the solid is easily seen to be entirely due to the elastic lattice. The data indicate little or no temperature effect in the liquid state. The sharp decrease of thermal conductivity at the melting point from the solid to the liquid condition has not been explained.

In a solid each atom vibrates about a mean position (which is fixed) independently of the remaining atoms. In a liquid the atoms vibrate about mean positions which while not fixed move with velocities small compared with the velocity of the order of magnitude  $\sqrt{\frac{KT}{m}}$  with which the atoms vibrate. This simple picture<sup>3</sup> of a liquid near its melting point has furnished valuable information regarding the physical properties of the liquid near the melting point.

Guggenheim and Fowler<sup>4</sup> have shown that if there are  $N$  positions of minimum potential energy in the quasi-crystalline liquid and that if each atom moves about a position of minimum potential energy in a field corresponding to an isotropic three-dimensional harmonic oscillator of frequency  $\nu_l$  and if the corresponding frequency in the solid is denoted by  $\nu_s$ , the entropy of melting is given by

$$\frac{\lambda_m}{T_m} = 3 K_0 \log \frac{\nu_s}{\nu_l} + K_0$$

where  $\lambda_m$  is the molecular heat of melting,  $T_m$  the melting temperature,  $K_0$  the Boltzman constant. The expression given above is based on the assumption amongst others that the vibrations are effectively classical, *i.e.*, that the temperature of melting  $T_m$  should be large compared with the characteristic temperature  $\frac{h\nu}{K_0}$ . Mott and Gurney have pointed out that it is only a rough approximation to retain the extra factor  $e$  in the partition function  $\{\Omega(T)\}^N$  as

has been done by Eyring. The true factor is not a constant but varies with temperature becoming more nearly unity near the melting point. In that case the term  $K_0$  in the above equation will fall to a very small fraction of  $K_0$  and the factor containing  $\frac{v_s}{v_l}$  becomes more important. Mott<sup>7</sup> has applied these considerations to explain the change in electrical conductivity on melting according to the modern theory of electronic conduction in metals.

According to Bloch<sup>6</sup>, in a pure metal the electrons move to a first approximation without resistance amongst the ions which are vibrating in an irregular fashion. It is only to a second approximation that there is any interaction between electrons and lattice vibrations so that the conduction of heat is a second-order effect. Further, it is shown by Bloch that a finite free path is caused by the heat motions of the lattice, so that the free path is reduced by raising the temperature. According to this view all the electrons in a metal are free but it does not follow that they are all conduction electrons. Actually the free electrons in a solid form open and closed groups in much the same way as do electrons in an atom and it is only when there are open groups that conduction electrons exist. In this way it is possible to arrive at a theory of thermal conduction which embraces both metals and semi-conductors. The conductivity depends on the extent to which the electrons may be considered free, *i.e.*, to the ease with which they move from atom to atom under the influence of the temperature gradient.

According to Bethe<sup>7</sup> the thermal conductivity at fairly high temperatures is given by

$$K = \frac{\pi^2}{3} \left( \frac{K_0}{e} \right)^2 \frac{2n_0}{\pi^2} \frac{M}{m} \frac{K'}{C} \left( \frac{dE}{dK'} \right)^2 \frac{1}{hK'a_0} K_0 \Theta^2.$$

Here  $n_0$  denotes the number of free electrons per atom,  $M$  and  $m$  the mass of the vibrating atom and the electron respectively,  $a_0$  the radius of the first Bohr orbit,  $K'$  denotes the wave number of an electron at the top of the Fermi-distribution,  $E$  the kinetic energy of such an electron,  $C$  is a constant depending on the interaction between the metallic ion and a free electron which is a property of the ion rather than the crystal structure.  $K'$  depends only on the specific volume and so will not alter appreciably on melting.  $\Theta$  is the characteristic temperature. In the expression for the thermal conductivity the quantities which change when melting takes place are  $K' \frac{dE}{dK'}$  and  $\Theta$ . The change in  $K' \frac{dE}{dK'}$  is comparatively small since the volume change is at most five per cent. for it can be shown that  $K' \frac{dE}{dK'}$  is nearly twice the maximum energy of the Fermi-distribution and this depends only on the volume. Hence any change in the thermal conductivity

from the solid to the liquid must be attributed to a change in  $\Theta$ . Bidwell's experiments show that the conductivity at the melting point is almost entirely electronic. Hence we write for  $K$  at the melting point the expression

$$K = \pi^2 \left( \frac{K_0}{e} \right)^2 \frac{2n_0 M}{\pi^2 m} \frac{K'}{C} \left( \frac{dV}{dK'} \right)^2 \frac{1}{hK_0 a_0} K_0 \Theta^2.$$

The change in thermal conductivity on melting is therefore given by

$$\frac{K_s}{K_l} = \left( \frac{v_s}{v_l} \right)^2 = \frac{2}{e^3} \frac{\lambda_m}{K_0 T_m}.$$

Table 1 shows the extent to which the hypothesis is in agreement with experiment.

Element	$N\lambda_m$ (Cal./mole)	$T_m$ °K	$\frac{T_m}{\Theta}$	$\frac{K_s}{K_l}$ (calc.)	$\frac{K_s}{K_l}$ (obs.)
Zinc	1700	692	2.9	2.23	2.01
Aluminium	1910	933	2.3	1.80	1.65
Lead	1120	590	6.6	1.88	1.78
Tin	(not accurate)	505	—	2.81	1.79
Sodium	630	370	1.85	1.58	1.33
Antimony	1660	903	—	5.65	1.14
Bismuth	2600	544	—	4.95	0.44

Aluminium, lead and sodium crystallize in the cubic form. Tin is tetragonal body-centered, zinc is hexagonal. Antimony and bismuth are well known to be of complex crystalline structure and so do not invalidate the suggestion put forward. These metals are always exceptional as compared with others. For instance the ratio of electrical resistance of solid to that of the liquid is about 0.5 as compared to values in the neighbourhood of 2 for other metals. It is well known that bismuth contracts on melting in contradistinction to other metals. It is also found that the velocity of sound<sup>8</sup> in liquid bismuth is greater than the velocity in solid bismuth in the neighbourhood of the melting point in contradistinction to other metals. Excluding the case of antimony and bismuth the agreement between calculated and observed values is fair. The lower conductivity in the liquid is due to the greater amplitude of the atomic oscillations and not to any extent to the irregularity of the arrangement of the atoms as contrasted with regular arrangement in the crystalline solid. For sodium and aluminium, the assumptions on which the calculation is based,

namely that  $T_m$  is greater than  $\frac{hv}{K_0}$ , is hardly justified and hence the more correct expression

$$\frac{e^{h\nu_s}}{e^{K_0 T_m} - 1} = \frac{1}{e^{3\frac{\lambda_m}{K_0 T_m}}} \frac{e^{h\nu_l}}{e^{K_0 T_m} - 1}$$

is used for the ratio of  $\frac{\nu_s}{\nu_l}$  in the table. As regards the values of  $\frac{k_s}{k_l}$ , the values are taken from Konno's<sup>9</sup> paper (the only data found in the literature). The drop in conductivity at the melting point found by Bidwell in the case of zinc agrees with the data of Konno.

If the decrease of thermal conductivity in liquid metals is due entirely to the change in the value of  $\nu$ , the thermal conductivity ought still to be independent of temperature. It is found that the values of thermal conductivity in the liquid state decrease slightly with temperature. While Konno's data suggested this, his results did not extend far enough to prove it. But recent experiments of Bidwell prove beyond doubt a slight decrease of thermal conductivity. The slight decrease in the liquid phase might be ascribed to the disordered state of the liquid.

In conclusion, it gives me very great pleasure to record my thanks to Professor A. Venkata Rao Telang for his guidance during the progress of this work.

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